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(54) **Metal oxide film having minutely roughed surface and method of forming same on glass substrate.**

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a metal oxide film having a minutely roughed surface, which is useful as a base or interlayer film of multilayered films on a glass substrate, and a method of forming the same.

2. Description of the Prior Art

Often it is desired to form a metal oxide film having a minutely roughed surface as a base or interlayer film of multilayered films on a glass substrate. This metal oxide film has numerous micro-pits which are scattered on its surface, thereby making the film minutely roughed. With the provision of this metal oxide film, adhesion of the multilayered films to the glass substrate is substantially enhanced, thereby improving abrasion resistance and durability of the multilayered films.

There are conventional methods of minutely roughening or forming numerous micro-pits on a metal oxide film. One example of the methods is etching a metal oxide film surface with hydrofluoric acid, fluorine nitrate or the like. However, this method has the following drawbacks.

Hydrofluoric acid and fluorine nitrate are very hazardous against human body. Therefore, these compounds must be handled very cautiously. This lowers the production efficiency. Furthermore, it is difficult to precisely control the thickness of a metal oxide film and the size of micro-pits.

Another example of the above conventional methods is producing numerous micro-pits on a metal oxide film by the thermal decomposition of an organic polymer added to a metal alkoxide solution. However, this method has the following drawback.

Micro-pits on the metal oxide surface tend to disappear by the densification of the film after baking at a temperature not lower than 400 °C.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a metal oxide film having a minutely roughed surface which is scattered with numerous and durable micro-pits.

It is another object of the present invention to provide an improved method of forming the metal oxide film on a glass substrate, which is free of the above-mentioned drawback.

According to a first aspect of the present invention, there is provided a method of forming on a glass substrate a metal oxide film having numerous micro-pits thereon, the method including the sequential steps of:

(a) preparing at least two sols respectively from at least one compound so as to disperse therein at least two polymers of the at least one compound, the at least one compound being selected from the group consisting of metal alkoxides and metal acetylacetonates, the at least two polymers having different average molecular weights;

(b) mixing the at least two sols with a solvent so as to prepare a coating solution;

(c) applying the coating solution to the glass substrate so as to form thereon a sol film; and

(d) heating the glass substrate so as to transform the sol film into a gel film and to form thereon numerous micro-pits.

According to a second aspect of the present invention, there is provided a metal oxide film which is prepared in accordance with the above method.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photograph taken through a tunnel microscope, showing a surface condition of a metal oxide film coated on a glass plate in accordance with the present invention;

Fig. 2 is a photograph taken through a scanning electron microscope of 10,000 magnifications, showing a surface condition of a metal oxide film coated on a glass plate in accordance with the present invention; and

Fig. 3 is a photograph similar to Fig. 2, but showing a surface condition of a metal oxide film which is coated on glass plate by a conventional method.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, there is provided a method of forming a metal oxide film on a glass substrate. This method includes the sequential steps of:

(a) preparing at least two sols respectively from at least one compound so as to disperse therein at least two polymers of the at least one compound, the at least one compound being selected from the group consisting of metal alkoxides and metal acetylacetonates, the at least two polymers having different average molecular weights;

(b) mixing the at least two sols with a solvent so as to prepare a coating solution;

(c) applying the coating solution to the glass substrate so as to form thereon a sol film; and

(d) heating the glass substrate so as to transform the sol film into a gel film and to form thereon numerous micro-pits.

A metal alkoxide sol and/or a metal acetylacetonato sol is used in the present invention because of the following reasons.

The average molecular weight of polymer of each sol can be relatively easily controlled. Furthermore, a metal oxide film made from a metal alkoxide sol and/or a metal acetylacetonato sol is high in transparency, hardness and durability. Still furthermore, a metal alkoxide and a metal acetylacetonato are relatively cheap in price and easily available.

A metal alkoxide of the present invention may be either a simple alkoxide having no organic group other than alkoxyl group, such as a methoxide, an ethoxide, an isopropoxide or the like, or an alkyl alkoxide having at least one alkyl group besides alkoxyl group, such as a monomethylalkoxide or a monoethylalkoxide.

A metal acetylacetonate of the present invention may be either a simple acetylacetonate having no organic group other than acetylacetone group, or an acetylalkoxyacetonate such as methylalkoxyacetonate or ethylalkoxyacetonate.

It is preferable to use Si, Ti and/or Zr as a metal of the metal alkoxide or of the metal acetylacetonate. Thus, examples of the metal alkoxides and the metal acetylacetonate are tetramethoxysilane, tetraethoxysilane, methyltrimethoxysilane, titanium tetraisopropoxide, titanium acetylacetonato, zirconium n-butoxide, zirconium acetylacetonato, dimethyldiethoxysilane, dimethyldimethoxysilane, titanium tetra-n-butoxide, zirconium tetraisopropoxide and zirconium tetraoctyrate.

In the present invention, at least two sols are used for the purpose of making the metal oxide film minutely rough. At least two polymers which are respectively dispersed in the at least two sols have different average molecular weights.

In the present invention, at least one compound selected from the group consisting of metal alkoxides and metal acetylacetonates is used for preparing the at least two sols.

In the present invention, it is preferable to use one sol containing the polymer having an average molecular weight ranging from about 800 to about 8000 and more preferably from about 2000 to about 7000, and the other at least one sol containing the polymer having an average molecular weight not lower than 10,000 and more preferably from 10,000 to about 70,000 or from about 100,000 to about 400,000.

The average molecular weights of the polymers can be relatively easily controlled by adjusting hydrolysis reaction or polycondensation reaction of a metal alkoxide and/or a metal acetylacetonate. In fact, this adjustment can be conducted by selecting a suitable catalyst, for example, from hydrochloric acid, nitric acid and acetic acid, and controlling the amount of the catalyst, pH value, the reaction temperature, etc. It is preferable to use a pH value of a metal alkoxide or metal acetylacetonato sol, ranging from about 1 to about 6, more preferably from about 2 to about 4. The reaction temperature of hydrolysis and polycondensation preferably ranges from about 20 °C to about 80 °C, and more preferably from 25 °C to about 70 °C. It may be difficult to set fixed conditions with respect to the type of catalyst, pH value, the reaction temperature, etc. for different combinations of sols.

It is preferable to mix the above-mentioned one sol with the other at least one sol in the ratio of 1:1 to 8:1, more preferably from 3:1 to 6:1, by the number of moles of solute calculated as metal oxide basis.

It is preferable to have a coating solution having a concentration of a metal alkoxide and/or a metal acetylacetonate in an alcohol solution in the range from 0.1 to 10 wt%. If the concentration is less than 0.1 wt%, it is difficult to form uniformly scattered micro-pits on the surface of the metal oxide film. If the concentration is higher than 10 wt%, the solution becomes too viscous. This tends to form cracks on the surface of the metal oxide film. As the alcohol solution, it is usual to use methyl alcohol, isopropyl alcohol or 1-butanol.

It is preferable to adjust viscosity of the coating solution in the range from 1 to 10 cP.

As the coating method, it is usual to use dip coating, spraying, flow coating or spin coating.

It is preferable to dry each coated film at a temperature of about 100 °C for about 30 min so as to transform the coated film into a gel film having numerous scattered micro-pits thereon.

It should be noted that the scattered micro-pits according to the present invention will not disappear even if the metal oxide film is baked at a temperature not lower than 500 °C.

A glass substrate according to the present invention may be colorless or colored as long as it is transparent. The glass substrate may be flat or curved in shape, or a tempered one.

The advantages of the present invention will be described in the following.

Even if a glass substrate coated with a metal oxide film in accordance with the present invention is baked at a high temperature, for example, not lower than 500 °C, numerous micro-pits are stable and will not disappear. Therefore, adhesion of the metal oxide film to the glass substrate is substantially enhanced. Furthermore, adhesion between the metal oxide films of a laminated films is also enhanced. It should be noted that the metal oxide

film is high in transparency and hardness.

The following examples are illustrative of the present invention.

Example 1

In this example, three-layered metal oxide films were formed on a glass substrate in accordance with the following steps.

Firstly, a clear float glass plate 300 mm square in widths and 5 mm in thickness was washed with neutral detergent, then with water and then with an alcohol. Separately, a first silicon ethoxide sol was prepared, such that polymer in the sol had an average molecular weight of about 5,700. A second silicon ethoxide sol was prepared, such that polymer in the sol had an average molecular weight of about 350,000. Then, 100 ml of the first silicon ethoxide sol and 50 ml of the second silicon ethoxide sol were mixed with 200 ml of isopropyl alcohol and 100 ml of 1-butanol in a beaker so as to make a coating solution. The coating solution was stirred for about 30 min, and its viscosity was adjusted to about 2 cP. The coating solution was applied to the glass plate by a dip coating. Then, the thus coated glass plate was heated at a temperature, of about 200 °C for about 30 min, so as to form a gel film on the glass plate. With this, the gel film, i.e. a SiO_2 film as a first layer having a thickness of about 60 nm was formed. As shown in Figs. 1 and 2, numerous micro-pits were observed on the first layer with using a tunnel microscope of SEIKO ELECTRONICS Co. and a scanning electron microscope.

Then, a second layer was formed on the first layer in accordance with the following steps.

A titanium isopropyl alcohol sol was prepared, such that polymer in the sol had an average molecular weight of about 4,000. An isopropyltitanate sol was prepared, such that polymer in the sol had an average molecular weight of about 110,000. Then, 100 ml of the titanium isopropyl alcohol sol and 50 ml of the isopropyltitanate sol were mixed with 200 ml of isopropyl alcohol and 100 ml of ethanol in a beaker, so as to form a coating solution. This coating solution was stirred for about 30 min, and its viscosity was adjusted to about 2 cP. The coating solution was applied to the first SiO_2 film surface by the dip coating. The thus coated glass plate was heated at a temperature of about 200 °C for about 30 min. With this, a gel film, i.e. a TiO_2 film as a second layer having a thickness of about 70 nm was formed. Numerous micro-pits were also observed on the second layer with using the above-microscopes.

Then, a third layer was formed on the second layer in accordance with the following steps.

A silicon ethoxide sol was prepared, such that polymer in the sol had an average molecular weight of about 5,700. 100 ml of the silicon ethoxide sol was added to 200 ml of ethanol in a beaker, so as to produce a coating solution. This coating solution was stirred for about 30 min, and its viscosity was adjusted to about 2 cP. The coating solution was applied to the second layer by the dip coating. The thus coated glass plate was heated at a temperature of about 200 °C for about 30 min. With this, a gel film, i.e. a SiO_2 film as a third layer having a thickness of about 100 nm was formed. A smooth surface of the third layer having no micro-pits thereon was observed with using the above microscopes.

Viscosity of each of the above-mentioned coating solutions was adjusted to about 2 cP.

The thus formed glass plate having the three-layered films thereon was heated at a temperature of about 600 °C for about 40 min. Then, the adhesion strength test was conducted on the three-layered films by the cross-cut adhesion test according to JIS K 5400. The result indicated by the number of no peel areas among 100 areas tested with cellophane tape was 100/100. That is, none of 100 areas peeled off, which shows a good adhesion strength.

The average molecular weights of the above-mentioned polymers were determined, as reduced to polystyrene, with using a gas permeation chromatography machine called SHODEX which is a trade name of SHOWA DENKO Co.

EXAMPLE 2

In this example, five layered films were formed on a glass plate in accordance with the following steps.

The first (SiO_2) and second (TiO_2) layers were formed in the same manner as those of Example 1 were. Then, a third (SiO_2) layer was formed on the second layer in the same manner as the first layer of Example 1 was. Then, a fourth layer was formed in accordance with the following steps.

A first zirconium acetylacetonato sol was prepared, such that polymer in the sol had an average molecular weight of about 4,500. A second zirconium acetylacetonato sol was prepared, such that polymer in the sol had an average molecular weight of about 110,000. 100 ml of the first sol and 100 ml of the second sol were mixed with 100 ml of isobutanol and 200 ml of ethanol in a beaker so as to form a coating solution. This coating solution was stirred for about 30 min, and its viscosity was adjusted to about 2 cP. Then, the coating solution was applied to the third (SiO_2) layer by the dip coating. The thus coated glass plate was heated at a temperature of about 200 °C for 30 min. With

this, a gel film as a fourth layer, i.e. a ZrO_2 film having a thickness of about 50 nm was formed. Then, a fifth layer was formed on the fourth layer in the same manner as the third layer of Example 1 was.

The surface condition of the fourth layer (ZrO_2 film) was observed with using the above microscopes. With this, the existence of numerous micro-pits were confirmed thereon.

The thus formed glass plate having the fifth-layered films thereon was heated at a temperature of about 600 °C for about 40 min. Then, the same adhesion strength test as that of Example 1 was conducted on the fifth-layered films. The result was 100/100.

COMPARATIVE EXAMPLE 1

In this comparative example, three-layered films were formed on a glass plate in accordance with the following steps.

A silicon ethoxide sol was prepared, such that polymer in the sol had an average molecular weight of about 100,000. Then, 100 ml of the silicon ethoxide sol was mixed with 200 ml of ethanol and 100 ml of 1-butanol in a beaker, so as to form a coating solution. This coating solution was stirred for about 30 min, and its viscosity was adjusted to about 2 cP. Then, the coating solution was applied to the glass plate by the dip coating. The thus coated glass plate was heated at a temperature of about 200 °C for about 30 min. With this, a gel film of SiO_2 layer having a thickness of about 60 nm and a smooth surface was formed on the glass plate. Then, a second layer was formed on the first layer in accordance with the following steps.

An isopropyltitanate sol was prepared, such that polymer in the sol had an average molecular weight of about 4,000. Then, 100 ml of the isopropyltitanate sol was mixed with 200 ml of isopropyl alcohol and 100 ml of ethanol in a beaker, so as to make a coating solution. The coating solution was stirred for about 30 min, and adjusted to have a viscosity of about 2 cP. Then, the coating solution was applied to the first layer by the dip coating. The thus coated glass plate was heated at a temperature of about 200 °C for about 30 min. With this, a gel film as a second layer, i.e. a TiO_2 film having a thickness of about 70 nm was formed. Then, a third layer of SiO_2 film having a thickness of about 100 nm was formed on the second layer in the same manner as the first layer of this comparative example was. Then, the thus formed glass plate having the three-layered films thereon was heated at a temperature of about 600 °C for about 40 min. Then, the same adhesion strength test as that of Example 1 was conducted on the three-layered films. The result was 78/100. That is, all the three layers in 78 areas remained on the glass plate. In more detail, peeling occurred in 10 areas at an interface between the second and third layers, and in 12 areas at an interface between the first and second layers.

COMPARATIVE EXAMPLE 2

In this comparative example, fifth-layered films were formed on a glass plate in accordance with the following steps.

First (SiO_2), second (TiO_2) and third (SiO_2) layers were formed on the glass plate in the same manner as the first, second and third layers of Comparative Example 1 were respectively. Then, a fourth layer was formed in accordance with the following steps.

A zirconium acetylacetonato sol was prepared, such that polymer in the sol had an average molecular weight of about 4,500. 100 ml of this sol was mixed with 200 ml of ethanol and 100 ml of butanol in a beaker so as to make a coating solution. This coating solution was stirred for about 30 min, and adjusted to have a viscosity of about 2 cP. Then, the coating solution was applied to the third layer by the dip coating. The thus coated glass plate was heated at a temperature of about 200 °C for about 30 min. With this, a gel film as a fourth layer, i.e. a ZrO_2 film of a thickness of about 50 nm was formed. Then, a fifth layer of SiO_2 film was formed on the fourth layer in the same manner as the third layer of Comparative Example 1 was. Then, the thus formed glass plate having the fifth-layered films thereon was heated at a temperature of about 600 °C for about 40 min. Then, the same adhesion strength test as that of Example 1 was conducted. The result was 83/100. That is, all the five layers in 83 areas remained on the glass plate. In more detail, peeling occurred in 10 areas at an interface between the fourth and fifth layers, and in 7 areas at an interface between the third and fourth layers.

Claims

1. A method of forming on a glass substrate a metal oxide film having numerous micro-pits thereon, the method comprising the steps of:
   (a) preparing at least two sols respectively from at least one compound so as to disperse therein at least two polymers of said at least one compound, said at least one compound being selected from the group consisting of metal alkoxides and metal acetylacetonates, said at least two polymers having different average molecular weights;
   (b) mixing said at least two sols with a solvent so as to prepare a coating solution;

(c) applying the coating solution to the glass substrate so as to form thereon a sol film; and
(d) heating the glass substrate so as to transform the sol film into a gel film and to form thereon numerous micro-pits.

2. A method according to Claim 1, wherein said solvent is an alcohol solution.

3. A method according to Claim 1, wherein the glass substrate is heated at step (d) at a temperature not lower than 100 °C.

4. A method according to Claim 1, wherein said at least one compound is selected from the group consisting of alkoxides of Si, Ti and Zr and acetylacetonates of Si, Ti and Zr.

5. A method according to Claim 1, wherein one polymer of said at least two polymers has an average molecular weight ranging from about 800 to about 8000, and the other at least one polymer of said at least two polymers has an average molecular weight not lower than 10,000.

6. A method according to Claim 5, wherein the other at least one polymer has an average molecular weight ranging from 10,000 to about 70,000.

7. A method according to Claim 5, wherein the other at least one polymer has an average molecular weight ranging from about 100,000 to about 400,000.

8. A method according to Claim 1, wherein at step (b) said one polymer and the other at least one polymer are mixed in the ratio of 1:1 to 8:1 by the number of moles of solutes calculated as metal oxide.

9. A method according to Claim 8, wherein at step (b) said one polymer and the other at least one polymer are mixed in the ratio of 3:1 to 6:1 by the number of moles of solutes calculated as metal oxide.

10. A multi-layered film including at least one layer of a metal oxide film prepared in accordance with the method of claim 1.

11. A method according to Claim 1, wherein at step (b) viscosity of the coating solution is adjusted to 1-10 centipoises.

12. A metal oxide film coated on a glass substrate, the film having numerous micro-pits formed thereon, the film being prepared in accordance with a method comprising the steps of:
(a) preparing at least two sols respectively from at least one compound so as to disperse therein at least two polymers of said at least one compound, said at least one compound being selected from the group consisting of metal alkoxides and metal acetylacetonates, said at least two polymers having different average molecular weights;
(b) mixing said at least two sols with a solvent so as to prepare a coating solution;
(c) applying the coating solution to the glass substrate so as to form thereon a sol film; and
(d) heating the glass substrate so as to transform the sol film into a gel film and to form thereon numerous micro-pits.

Patentansprüche

1. Ein Verfahren, um auf einem Glassubstrat einen Metalloxidfilm mit zahlreichen Mikrogrübchen auf diesem auszubilden, wobei das Verfahren die Schritte aufweist:
(a) daß mindestens zwei Sole jeweils aus mindestens einer Komponente hergestellt werden, um in diesen mindestens zwei Polymere aus der mindestens eine Komponente zu dispergieren, wobei zumindest eine Komponente aus der Gruppe bestehend aus Metallalkoxiden und Metallacetylacetonaten ausgewählt wird, wobei die mindestens zwei Polymere unterschiedliche durchschnittliche Molekulargewichte haben;
(b) daß die mindestens zwei Sole mit einem Lösungsmittel gemischt werden, um eine Beschichtungslösung herzustellen;
(c) daß die Beschichtungslösung auf das Glassubstrat aufgetragen wird, um auf diesem einen Solfilm zu bilden; und
(d) daß das Glassubstrat erhitzt wird, um den Solfilm in einen Gelfilm umzuformen und auf diesem zahlreiche Mikrogrübchen auszubilden.

2. Ein Verfahren nach Anspruch 1, worin das Lösungsmittel eine Alkohollösung ist.

3. Ein Verfahren nach Anspruch 1, worin das Glassubstrat in dem Schritt (d) auf eine Temperatur nicht niedriger als 100 °C erhitzt wird.

4. Ein Verfahren nach Anspruch 1, worin die mindestens eine Komponente aus der Gruppe bestehend aus Alkoxiden von Si, Ti und Zr und

Acetylacetonaten aus Si, Ti und Zr ausgewählt wird.

5. Ein Verfahren nach Anspruch 1, worin ein Polymer der mindestens zwei Polymere ein durchschnittliches Molekulargewicht hat, das in dem Bereich von 800 bis etwa 8000 liegt, und daß das andere mindestens eine Polymer der mindestens zwei Polymere ein durchschnittliches Molekulargewicht von nicht niedriger als 10000 hat.

6. Ein Verfahren nach Anspruch 5, worin das andere mindestens eine Polymer ein durchschnittliches Molekulargewicht hat, das in dem Bereich von 10000 bis etwa 70000 liegt.

7. Ein Verfahren nach Anspruch 5, worin das andere mindestens eine Polymer ein durchschnittliches Molekulargewicht hat, daß in dem Bereich von etwa 100000 bis etwa 400000 liegt.

8. Ein Verfahren nach Anspruch 1, worin bei Schritt (b) das eine Polymer und das andere mindestens eine Polymer in dem Verhältnis von 1:1 bis 8:1 in der Molanzahl des Lösungsprodukts berechnet als Metalloxid gemischt werden.

9. Ein Verfahren nach Anspruch 8, worin bei dem Schritt (b) das eine Polymer und das andere mindestens eine Polymer in dem Verhältnis von 3:1 bis zu 6:1 in der Molanzahl des Lösungsprodukts berechnet als Metalloxid gemischt werden.

10. Ein vielschichtiger Film mit mindestens einer Schicht aus einem Metalloxidfilm, der gemäß dem Verfahren von Anspruch 1 hergestellt wird.

11. Ein Verfahren nach Anspruch 1, worin bei dem Schritt (b) die Viskosität der Beschichtungslösung auf 1 bis 10 Zentipoise eingestellt wird.

12. Ein Metalloxidfilm, der auf einem Glassubstrat aufgebracht ist, wobei auf dem Film zahlreiche Mikrogrübchen ausgebildet sind, wobei der Film nach einem Verfahren hergestellt wird, das die Schritte aufweist:

(a) daß mindestens zwei Sole jeweils aus mindestens einer Komponente hergestellt werden, um in diesen mindestens zwei Polymere aus der mindestens eine Komponente zu dispergieren, wobei zumindest eine Komponente aus der Gruppe bestehend aus Metallalkoxiden und Metallacetylacetonaten ausgewählt wird, wobei die mindestens zwei Polymere unterschiedliche durchschnittliche Molekulargewichte haben;

(b) daß die mindestens zwei Sole mit einem Lösungsmittel gemischt werden, um eine Beschichtungslösung herzustellen;

(c) daß die Beschichtungslösung auf das Glassubstrat aufgetragen wird, um auf diesem einen Solfilm zu bilden; und

(d) daß das Glassubstrat erhitzt wird, um den Solfilm in einen Gelfilm umzuformen und auf diesem zahlreiche Mikrogrübchen auszubilden.

Revendications

1. Méthode de formation sur un substrat de verre d'un film oxyde métallique ayant de nombreux micro-puits sur lui, la méthode comprenant les étapes de :

(a) préparation d'au moins deux sols respectivement d'au moins un composé de façon à y disperser au moins deux polymères dudit au moins composé, ledit au moins un composé étant choisi dans le groupe consistant en des alcoxydes métalliques et des acétylacétonates métalliques, lesdits au moins deux polymères ayant différents poids moléculaires moyens;

(b) mélange desdits au moins deux sols avec un solvant de façon à préparer une solution de revêtement;

(c) application de la solution de revêtement au substrat en verre de façon à former sur celle-ci un film de sol; et

(d) chauffage du substrat en verre de façon à transformer le film de sol en un film de gel et pour former sur celui-ci de nombreux micro-puits.

2. Méthode selon la revendication 1, dans laquelle ledit solvant est une solution d'alcool.

3. Méthode selon la revendication 1, dans laquelle le substrat en verre est chauffé à l'étape (d) à une température non inférieure à 100 • C.

4. Méthode selon la revendication 1, dans laquelle au moins un composé est choisi dans le groupe consistant des alcoxydes de Si, de Ti et de Zr et des acétylacétonates de Si, Ti et Zr.

5. Méthode selon la revendication 1, dans laquelle un polymère desdits au moins deux polymères a un poids moléculaire moyen dans l'intervalle d'environ 800 à environ 8000, et l'autre au moins un polymère desdits au moins deux

polymères a un poids moléculaire moyen non inférieur à 10 000.

6. Méthode selon la revendication 5, dans laquelle l'autre au moins un polymère a un poids moléculaire moyen dans l'intervalle de 10 000 à environ 70 000.

7. Méthode selon la revendication 5, dans laquelle l'autre au moins un polymère a un poids moléculaire moyen dans l'intervalle entre environ 100 000 et environ 400 000.

8. Méthode selon la revendication 1, dans laquelle à l'étape (b) ledit un polymère et l'autre au moins un polymère sont mélangés dans le rapport de 1:1 à 8:1 en nombre de moles de solutés calculé en tant qu'oxyde métallique.

9. Méthode selon la revendication 8, dans laquelle à l'étape (b) ledit un polymère ou l'autre au moins un polymère sont mélangés dans le rapport de 3:1 à 6:1 en nombre de moles de solutés calculé en tant qu'oxyde métallique.

10. Film multi-couche incluant au moins une couche d'un film d'oxyde métallique préparé selon la méthode de la revendication 1.

11. Méthode selon la revendication 1, dans laquelle à l'étape (b) la viscosité de la solution de revêtement est ajustée à 1-10 centipoises.

12. Film d'oxyde métallique recouvert sur un substrat en verre, le film ayant de nombreux micropuits formés sur lui, le film étant préparé selon une méthode comprenant les étapes de :

(a) préparation d'au moins deux sols respectivement d'au moins un composé de façon à y disperser au moins deux polymères dudit au moins un composé, ledit au moins un composé étant choisi dans le groupe consistant des alcoxydes métalliques et des acétylacétonates métalliques, lesdits au moins deux polymères ayant différents poids moléculaires moyens;

(b) mélange desdits au moins deux sols avec un solvant de façon à préparer une solution de revêtement;

(c) application de la solution de revêtement au substrat de verre de façon à former sur lui un film de sol; et

(d) chauffage du substrat en verre de façon à transformer le film de sol en film de gel et pour former sur lui de nombreux micropuits.

FIG.1

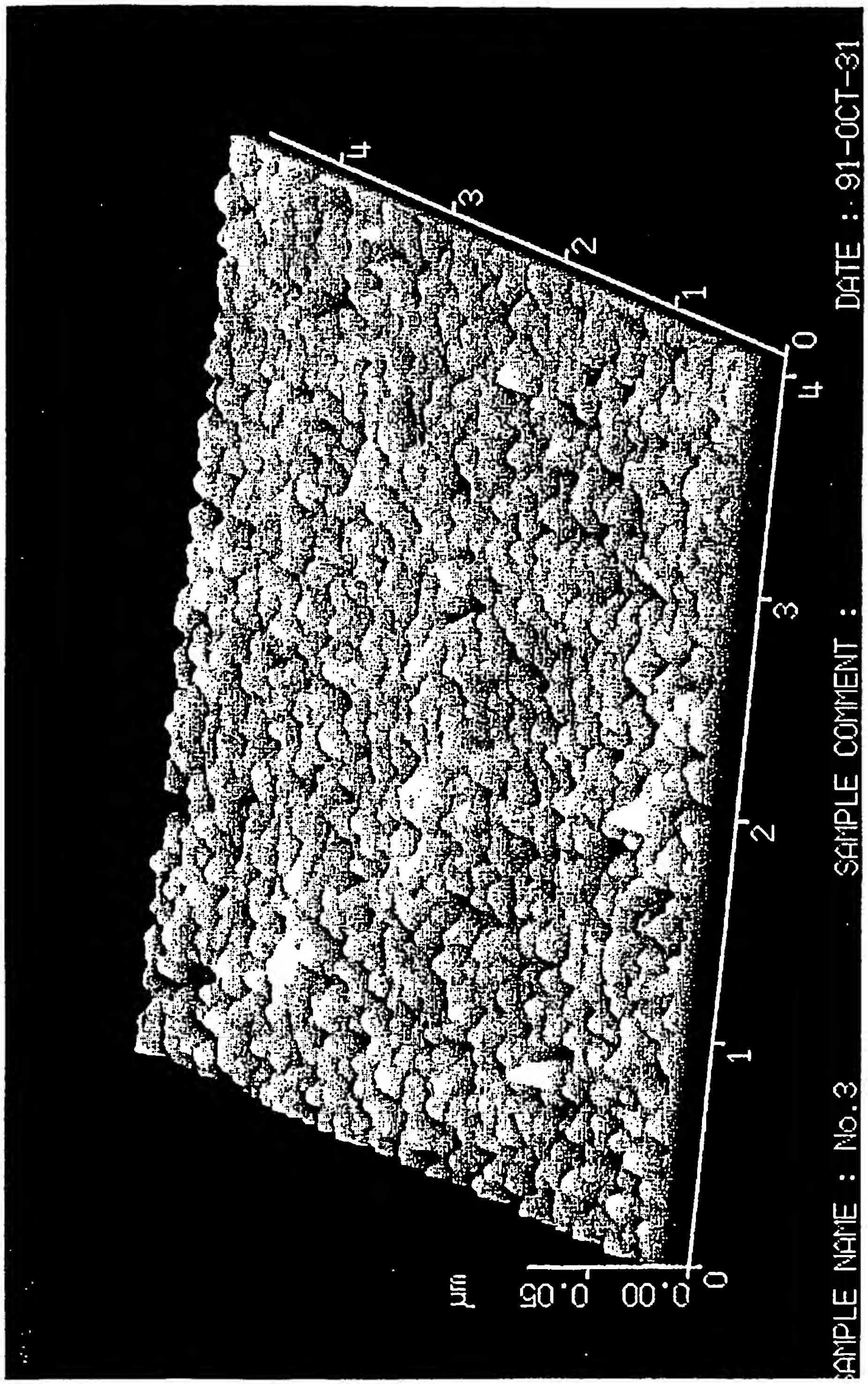
µm
0.05
0.00
0
1
2
3
4
0
1
2
3
4
SAMPLE NAME : No.3
SAMPLE COMMENT :
DATE : 91-OCT-31

FIG.2

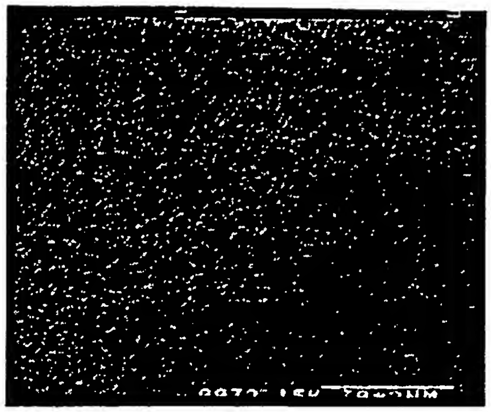

FIG.3
(PRIOR ART)